A student-oriented derivation of a reliable equation of state for a hard-disc fluid

Mariano López de Haro, Andrés Santos and Santos Bravo Yuste

† Centro de Investigación en Energía, Apartado Postal 34, Temixco, Mor. 62580, Mexico

‡ Departamento de Física, Universidad de Extremadura, E-06071 Badajoz, Spain

Abstract. The 'derivation' in a standard course in statistical thermodynamics of a very simple equation of state for a hard-disc fluid is discussed. This equation has the form of a simple rational function that fulfils the requirements of being exact to first order in density and containing a (single pole) singularity at the close-packed density. This approach is in the same spirit as that used by Boltzmann in 1898 to propose an equation of state for hard spheres.

1. Introduction and historical perspective

On a first contact with the subject, students of introductory courses in statistical thermodynamics sometimes get the impression that, other than for ideal systems, very few interesting results may be derived analytically. As a consequence, many theoretical approaches are regarded as merely formal and it is often assumed that simplicity and accuracy are conflicting concepts. Therefore, examples and simple models in which such beliefs can clearly be ruled out are certainly very valuable. The main aim of this paper is to present one such example in the case of classical fluids. As an extra point, we would like to convey the idea that a combination of physical intuition, available evidence and not very sophisticated mathematics may (albeit with some luck!) work in providing further examples.

One remarkable case of this approach, obtained mostly by intuitive reasoning, but giving an essentially qualitatively correct picture of the thermodynamic properties of gases and liquids, is the famous van der Waals's equation of state. Its derivation relies heavily on the molecular view of matter and on a tremendous insight into the fundamental physics of the liquid state. As van der Waals had already realized, his equation is only a first approximation to the equation of state of fluids, and therefore many other empirical or semi-theoretical attempts have been made [1, 2] to improve van der Waals's equation. For the sake of simplicity and also for gaining insight through analytical derivations, most of the proposals have referred to systems of particles with a hard core.

The virial expansion, first introduced by Kamerlingh Onnes [2] as a mathematical representation of experimental data on the equation of state, is an expansion that gives the deviation from ideal gas behaviour in ascending powers of the density:

$$Z \equiv p/\rho kT = 1 + B_2\rho + B_3\rho^2 + \cdots \tag{1}$$

where p is the pressure, ρ the number density, k the Boltzmann constant and T the absolute temperature. The successive virial coefficients B_n, which in general depend on the temperature, are related to the interactions of isolated groups of $n = 2, 3, \ldots$, molecules by exact statistical-mechanical formulae. As with any power series, a knowledge of the region of density in which the virial series converges is important for its use. Again hard-core systems are often used for clarification. In the case of hard rods of length σ in a line, the exact equation of state was obtained independently by Rayleigh [3] and Korteweg [4] in 1891 and rederived much later by Herzfeld and Goeppert-Mayer [5] and Tonks [6]; in this case, $B_n = \sigma^n$, so that the virial series converges for the whole physical domain $0 < \rho\sigma < 1$ and there is no phase transition. On the other hand, the exact equation of state for the hard-sphere system (and its two-dimensional analogue of hard discs) is not known. Computer simulations have shown that these systems can exist in two thermodynamically stable states corresponding to a fluid and a crystal, respectively. (There cannot be a gas–liquid transition in these purely hard-core systems because of the lack of an attractive part in the pair potential.) It has been suggested that the singularity that certainly must exist in the true equilibrium equation of state at the fluid–solid transition density might be associated with a divergence of the virial series. However, the very recent results on the eighth-order virial coefficients for hard spheres and hard discs [7] indicate that the virial series as given in equation (1) diverges at the crystalline close-packing limit [8], as suggested earlier by Baram and Luban [9].

It is of interest for our purposes to mention a little known contribution in connection with the equation of state in which Boltzmann's intuition is clearly manifested. This is an early attempt at what is now known as a (two-point) Padé approximant [10]. Boltzmann thought that the pressure would rise steadily, becoming infinitely large at the close-packing density, an idea already suggested by Korteweg [11]. So he proposed [12] the following equation for a hard-sphere fluid:

$$Z = \frac{1 + \frac{8}{3}\eta + \frac{14}{3}\eta^2}{1 - \frac{4}{3}\eta} \tag{2}$$

where $\eta = \frac{1}{6}\pi\rho\sigma^3$ is the packing fraction, i.e. the fraction of volume occupied by the molecules, and σ is the hard-sphere diameter. He rounded off the close-packing fraction value $\eta_{cp} = \frac{1}{6}\sqrt{2}\pi \simeq 0.7405$ as $\frac{3}{4}$ for simplicity. The coefficients in the numerator were determined by the condition that, on expansion, equation (2) yields the correct first, second, and third virial coefficients. It turns out that equation (2) also gives a good estimate of the then unknown fourth coefficient. Much later, and with the knowledge of higher virial coefficients, the same idea was taken up by Alder and Hoover [13], who suggested the use of approximants to the compressibility factor Z which force the equation of state to have a singularity (simple pole) at the close-packing density.

It is instructive and pertinent here to recall the controversy between Boltzmann and van der Waals on the correct value of the fourth virial coefficient [14]. After the kinetic theory of gases was developed, a key problem concerning the 'excluded volume' attracted the attention of nineteenth century physicists. It was thought that since molecules have a finite size, the actual volume of the container of a gas had to be corrected in the equation of state for the volume occupied by the molecules themselves. Van der Waals's arguments give only the first-order effect (second virial coefficient) of the deviation, that is, only through binary collisions. Later on, Boltzmann and Jäger independently calculated the value of the third virial coefficient for a hard-sphere gas, correcting the error made in a former calculation by van der Waals. Without any strict formalism to guide him (at the time the presently available expressions for the virial coefficients in terms of the intermolecular potential had not been derived) and realizing that a

further step with the same method was virtually impossible, Boltzmann went on to compute the fourth virial coefficient, which turned out to be at odds with the result derived by J J van Laar using a method suggested by van der Waals. It took a long time and the advent of new and powerful statistical-mechanical methods before Nijboer and van Hove [15] confirmed the correctness of Boltzmann's value, doing final justice to his outstanding degree of insight.

Since a liquid neither shows the absence of multiple interactions characteristic of the dilute gas nor possesses the ordered structure of a solid, the liquid state poses more difficulties in the quantitative application of the methods of statistical thermodynamics than either the solid state or the dilute gas. In fact, theories of the liquid state are sometimes distinguished as gas-like or solid-like, depending on whether the approximations involved are correct in the limit of the dilute gas, or in the limit of the solid, respectively [1]. Thus, one of the virtues of a proposal such as equation (2) and of the Alder–Hoover approximants is their attempt to satisfy both limits simultaneously. The same idea lies behind a recently proposed equation of state for a fluid of hard discs [16] and in the present paper we want to discuss how, on the basis of very simple calculations, its derivation can be introduced as an exercise when dealing with classical fluids in a standard course in statistical thermodynamics.

2. Didactic application

The equation of state for a hard-disc fluid can be used didactically to introduce the student to a sensible and attractive application of statistical-mechanical methods. The presentation easily fits into the scheme of standard textbooks. In fact, we will make some parallels with exercises of [17, chapter 7].

As is well known, by assuming that the potential energy of the fluid is pairwise additive, that the intermolecular potential $u(r)$ depends only upon the separation of the two molecules and that it goes to zero very rapidly in a few molecular diameters, the second virial coefficient B_2 is given by [17, 18]

$$B_2 = -\frac{1}{2} \int \mathrm{d}\boldsymbol{r} \left[\mathrm{e}^{-u(r)/kT} - 1 \right]. \tag{3}$$

A two-dimensional fluid of hard discs is perhaps the simplest model that exhibits many of the most important structural phenomena that occur in dense fluid systems found in nature. The potential energy in a hard-disc fluid has the form

$$u(r) = \begin{cases} \infty & r < \sigma \\ 0 & r > \sigma \end{cases} \tag{4}$$

where σ is the diameter of the discs. This potential has no attractive part, but does model the steep repulsive part of realistic potentials. The second virial coefficient for this system follows trivially after substitution of equation (4) into equation (3), namely $B_2^{\mathrm{hd}} = \frac{1}{2}\pi\sigma^2$ †.

Since the radius of convergence of the virial expansion is not known, it is hard to say what limiting density it approaches as the pressure becomes infinite, but the virial equation appears to have a pole at the close-packed density $\rho = \rho_{\mathrm{cp}}$ [8, 9]. It is not difficult to find the value of $\rho = \rho_{\mathrm{cp}}$ for a hard-disc fluid‡. Close-packed circular discs form a hexagonal array in two dimensions that fills a fraction $\eta_{\mathrm{cp}} = \frac{1}{6}\sqrt{3}\,\pi \simeq 0.9069$ of the space. This number follows from the ratio of the area of the disc of diameter σ to the area of the circumscribing hexagon whose side equals $\sigma/\sqrt{3}$. Since the packing fraction in two dimensions is $\eta = \frac{1}{4}\pi\rho\sigma^2$, it follows that $\rho_{\mathrm{cp}} = \frac{2}{3}\sqrt{3}\sigma^{-2}$ discs per unit area. It is interesting to point out that a slightly harder problem (since it deals with spheres rather than discs) is commonly proposed as an exercise in standard solid state textbooks [19].

---

† Note that exercise 7.13 in Chandler's book [17] could easily be modified to accommodate this calculation.
‡ See exercise 7.24 in [17].

Once we have determined the second virial coefficient B_2^{hd} and the close-packed density ρ_{cp}, we are in a position to derive an equation of state for the hard-disc fluid that, on the one hand, yields the correct dilute gas limit (through the value of B_2^{hd}), i.e. $Z = 1 + 2\eta + \cdots$, and on the other is forced to give a diverging pressure at $\rho = \rho_{\text{cp}}$, namely $Z \sim (\eta_{\text{cp}} - \eta)^{-1}$. In the spirit of Boltzmann's equation of state for hard spheres, equation (2), we choose to write the compressibility factor for hard discs as the rational function $Z = (1 + a\eta + b\eta^2)^{-1}$, so that the correct limiting behaviour both for the dilute gas and for the hexagonal close-packed solid is incorporated. This leads [16] to

$$Z_{[0,2]} = \frac{1}{1 - 2\eta + \eta^2(2\eta_{\text{cp}} - 1)/\eta_{\text{cp}}^2} \tag{5}$$

where the subscript $[0, 2]$ has been included to emphasize that the numerator is of zeroth order in η, while the denominator is of second order in the same variable. Equation (5) is clearly physically appealing, is analytical and simple, and yet it is accurate both with respect to the values of the third and up to the eighth virial coefficients and as compared to the simulation results of Erpenbeck and Luban [20], as shown in [16]. What is more important here is that the student can easily check the reliability of equation (5) against his/her own simulations†. In fact, we have used the BASIC Monte Carlo code provided in [17] to perform such a comparison‡. The results are displayed in figure 1, where we have also included the data from the more accurate simulation of [20]. The small discrepancy at $\rho/\rho_{\text{cp}} = 0.7$ is due to the crudeness of the present simulation. The agreement between equation (5) and the results by Erpenbeck and Luban at this density (as it is over all densities) is very good. It seems to us that a student can profit from being able to compare not only his/her simulation with those found in the specialized literature, but also these with a simple equation that he/she has previously 'derived'.

It could correctly be argued that the choice of the Padé approximant [0, 2] is to some extent arbitrary. As a matter of fact, with the same information a Padé approximant [1, 1] is equally plausible and more in the line of equation (2). The corresponding compressibility factor would then be

$$Z_{[1,1]} = \frac{1 + (2 - 1/\eta_{\text{cp}})\eta}{1 - \eta/\eta_{\text{cp}}}. \tag{6}$$

However, the reason for preferring equation (5) over equation (6) is that, on expanding both equations, the former gives a better estimate of the (exactly known) third virial coefficient, $B_3^{\text{hd}} = (\frac{1}{3}\pi^2 - \frac{1}{4}\pi\sqrt{3})\sigma^4$, than the latter§. The comparison between these two Padé equations of state could also be suggested as an exercise to the student in which he/she would have to decide on the 'quality' of each of them in terms of the prediction of higher order virial coefficients and the agreement with simulations.

3. Concluding remarks

In conclusion, in this paper we have presented a suggestive example in which, following an idea already proposed by Boltzmann in 1898 [12], an analytical equation of state for hard discs in the form of a rational function may easily be derived by a student using the second virial coefficient and the close-packing fraction as input. The accuracy of this equation may be

† See, for instance, exercises 7.33 and 7.34 in Chandler's book [17].

‡ See section 7.8 and pages 230–3 in [17]. In this code, the radial distribution function $g(r)$ of a system of 20 hard discs is evaluated at shells of thickness 0.10σ. Linear extrapolation yields the contact value $g(\sigma^+)$, which is directly related to the equation of state: $Z = 1 + 2\eta g(\sigma^+)$. In our simulations, we have averaged over 5000 passes and the maximum step size 'DEL' has been chosen so that the number of acceptances lies in the interval 25% to 65% for all densities.

§ From equation (5) one finds $B_3^{\text{hd}} = \left(\frac{1}{4}(\pi^2 + 3) - \frac{1}{4}\pi\sqrt{3}\right)\sigma^4$ (which deviates by 4% from the exact value), while equation (6) yields $B_3^{\text{hd}} = \frac{1}{4}\pi\sqrt{3}\sigma^4$ (which deviates by 30% from the exact value).
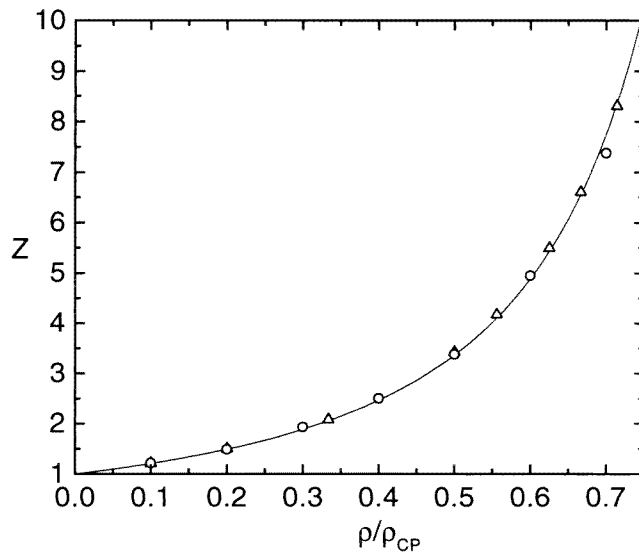
Figure 1. Compressibility factor for hard discs as a function of reduced density. The solid line corresponds to equation (5). Open circles represent the results obtained with the Monte Carlo code of [17], while open triangles correspond to the accurate simulation results of Erpenbeck and Luban [20].

assessed from a comparison (i) with simulation results reported in the literature [20] or, even better, obtained by the student using, for instance, the simple Monte Carlo code in Chandler's book [17], and (ii), after expansion, with the known values of the eight virial coefficients [7]. All this material may readily be incorporated as exercise work in an introductory course in statistical thermodynamics.

Acknowledgments

References

[1] Levelt J M H and Cohen E G D 1964 A critical study of some theories of the liquid state including a comparison with experiment *Studies in Statistical Mechanics* vol II, ed J de Boer and G E Uhlenbeck (Amsterdam: North-Holland) pp 107–239
[2] For references to the original sources and illuminating discussions about van der Waals's equation of state and the equation of state for hard spheres, see: Brush S G 1976 *The Kind of Motion We Call Heat* Books 1 and 2 (Amsterdam: North-Holland) chs 7 and 11
Rowlinson J S 1988 Van der Waals and the physics of liquids *Studies in Statistical Mechanics* vol XIV, ed J S Rowlinson (Amsterdam: North-Holland) pp 1–119
[3] Lord Rayleigh 1891 On the virial of a system of hard colliding bodies *Nature* **45** 80–2 (reprinted 1902 *Scientific Papers* vol 3 (Cambridge: The University Press) p 469)
[4] Korteweg D T 1891 On van der Waals's isothermal equation *Nature* **45** 152–4
[5] Herzfeld K F and Goeppert-Mayer M 1934 On the states of aggregation *J. Chem. Phys.* **2** 38–44
[6] Tonks L 1936 The complete equation of state of one, two, and three-dimensional gases of elastic spheres *Phys. Rev.* **50** 955–63

[7]   Janse van Rensburg E J 1993 Virial coefficients for hard discs and hard spheres *J. Phys. A: Math. Gen.* **26** 4805–18

[8]   Sanchez I C 1994 Virial coefficients and close-packing of hard spheres and disks *J. Chem. Phys.* **101** 7003–6

[9]   Baram A and Luban M 1979 Divergence of the virial series for hard discs and hard spheres at closest packing *J. Phys. C: Solid State Phys.* **12** L659–64

[10] Bender C M and Orszag S A 1978 *Advanced Mathematical Methods for Scientists and Engineers* (New York: McGraw-Hill) section 8.3

[11] Korteweg D I 1892 On van der Waals's isothermal equation *Nature* **45** 277

[12] Boltzmann L 1898 *Vorlesungen über Gastheorie* vol 2 (Leipzig: Barth) ch 5 (Engl. transl. Brush S G 1964 *Lectures on Gas Theory* (Berkeley, CA: University of California Press) pt 2, ch 5)

[13] Alder B J and Hoover W G 1968 Numerical statistical mechanics *Physics of Simple Liquids* edited by H N V Temperley, J S Rowlinson and G S R Rushbrooke (Amsterdam: North-Holland) pp 79–113

[14] For an interesting account on this question, see: Nairn J H and Kilpatrick J E 1972 Van der Waals, Boltzmann, and the fourth virial coefficient of hard spheres *Am. J. Phys.* **40** 503–15 and references therein

[15] Nijboer B R A and van Hove L 1952 Radial distribution function of a gas of hard spheres and the Superposition Approximation *Phys. Rev.* **85** 777–83

[16] Yuste S B, López de Haro M and Santos A 1995 An accurate and simple equation of state for hard disks *J. Chem. Phys.* **103** 4622–5

[17] Chandler D 1987 *Introduction to Modern Statistical Mechanics* (Oxford: Oxford University Press)

[18] Reif F 1965 *Fundamentals of Statistical and Thermal Physics* (New York: McGraw-Hill)

[19] Kittel C 1966 *Introduction to Solid State Physics* 3rd edn (New York: Wiley) ch 1, problem 4
      Hall H E 1974 *Solid State Physics* (New York: Wiley) problem 1.8(c)
      Ibach H and Lüth H 1993 *Solid State Physics* (Berlin: Springer) problem 2.7

[20] Erpenbeck J J and Luban M 1985 Equation of state of the classical hard-disk fluid *Phys. Rev.* A **32** 2920–2